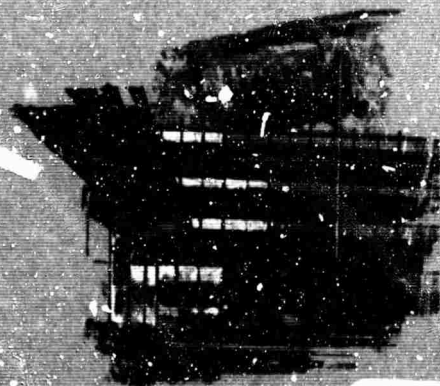


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ABSORPTION BY CO₂
BETWEEN 1800 AND 2850 cm⁻¹
(3.5-5.6 MICRONS)

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SCIENTIFIC REPORT

ABSORPTION BY CO₂ BETWEEN 1800 AND 2850 cm⁻¹
(3.5-5.6 Microns)

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ABSTRACT

Transmission spectra in the 1800-2850 cm^{-1} region have been obtained for more than 100 samples of CO_2 and CO_2 mixed with N_2 and A. The spectral resolution was 2.5 cm^{-1} . Sample pressures varied from 0.0055 to 742 torr with absorber thicknesses covering the range from 0.081 to 84,400 $\text{atm cm}^{\text{STP}}$. Spectra of several samples at the lower pressures show the effect of Doppler broadening. Measurements in the 2400-2560 cm^{-1} region provide information about the absorption by the extreme wings of collision-broadened lines. Replotted transmission spectra and extensive tables of integrated absorptance for 116 samples are included.

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SECTION 1

INTRODUCTION AND SUMMARY

Absorption and emission by CO_2 in the $1800\text{-}2850\text{ cm}^{-1}$ region plays a very important part in the transfer of heat in the atmospheres of the earth and other planets. Because of many very strong lines in this region, there is appreciable absorption by atmospheric paths which are so short or at such low pressures that absorption in other regions of the infrared is almost negligible.

Several quantitative measurements on the absorption in this region have been made previously with low resolution for the purpose of determining the relationship between the integrated absorptance $\int A(\nu) d\nu$ and the parameters, absorber thickness and pressure.^{1,2} The present investigation, which was undertaken to supplement the previous work, includes measurements on samples having much greater absorber thicknesses. Therefore, it has been possible to measure CO_2 absorption in spectral regions where it had not been observed previously. Other samples with long paths and very low pressures have provided data under conditions for which Doppler broadening of the absorption lines is important. Information on the absorption by the extreme wings of the strongest lines has also been obtained from measurements in the $2400\text{-}2560\text{ cm}^{-1}$ region.

The experimental methods are discussed in Section 2. Section 3 includes spectral curves for 116 samples of CO_2 alone and $\text{CO}_2 + \text{N}_2$ as well as a limited discussion of the results. Extensive tables of the integrated absorptance are included in Section 4. Tables of transmittance versus wavenumber are available from the authors for workers who require them.

Additional measurements with resolution less than 0.5 cm^{-1} will be made in this region by us in the future. The results will be used to identify many of the very weak bands and to determine the contributions of various bands in regions where several of them may overlap.

SECTION 2

EXPERIMENTAL

2.1 INSTRUMENTAL

Samples of CO_2 alone and mixtures of CO_2 with N_2 or A were contained in a multiple-pass absorption cell whose base length is approximately 29 meters. The cell was used at 4, 8, 16, and 32 passes, giving path lengths of 121, 237, 469, and 933 meters, respectively. Radiation from a Nernst glower traversed the absorption cell and formed an image of the source on the slit of a Perkin Elmer Model 112 spectrometer which employed an LiF prism and a thermocouple detector. While a spectrum was being scanned, the spectrometer slits were adjusted continuously by a string cam which coupled the slit micrometer to the Littrow screw that rotated the prism. The cam, which was designed and built in our laboratory, adjusted the slits so that the signal from the detector was approximately constant while scanning a spectrum with the absorption cell evacuated. The spectral slitwidth was approximately 2.5 cm^{-1} .

The monochromator was flushed with dry N_2 , and the remainder of the optical path outside the absorption cell was contained in vacuum tanks in order to eliminate absorption by atmospheric gases. Wavenumber calibration was obtained from H_2O , CO_2 , CH_4 , N_2O and CO absorption lines whose positions are known. Details of the multiple-pass cell and the spectrometer have been described previously.^{3,4}

2.2 SAMPLING PROCEDURE

The gases used for samples were obtained from commercial cylinders. The N_2 was high-purity dry grade with less than 10 parts H_2O per million,

and the CO_2 contained traces of H_2O and CO . It is probably safe to assume that all the isotopes were present in their natural abundances (C^{12} , 98.9%; C^{13} , 1.1%; O^{16} , 99.76%; O^{17} , 0.04%; O^{18} , 0.20%; H , 99.9844%; D , 0.0156%).

An Hg manometer was used to measure pressures in the range from 50 torr to 1 atm; a manometer containing a special oil was used for pressures between 1.5 and 50 torr. Some of the lower pressures were measured by a McLeod gauge; other pressures of pure CO_2 which were too low to measure accurately with any of the gauges were determined by expanding CO_2 into the cell from a cylinder filled to a pressure that could be measured accurately. The volume of the cylinder was approximately 0.001 times that of the absorption cell. The ratio of the pressure in the cylinder to the resulting pressure in the cell was determined by using enough CO_2 that the pressure in the cell was several torr, which was high enough to be measured accurately. We then assumed that the ratio of pressures was the same at lower pressures. When the initial pressure in the cylinder was greater than approximately 1 atm, it was necessary to account for the non-linearity in the relation between CO_2 density and pressure. From the Van der Waal's constants for CO_2 , we can show that the density is proportional to $p(1 + 0.005p)$ if p , the pressure in atm, is less than approximately 15.

Adsorption of CO_2 on the walls of the cylinder and the absorption cell probably gives rise to the greatest uncertainty in determining CO_2 pressures by the expansion method. If the percent adsorbed was independent of pressure, very little error was introduced. However, it seems possible that a greater percentage of gas would be adsorbed when it is first added until a film is formed on the surface; after this, the percentage adsorbed would decrease as the pressure increases. No measurements were made to determine if such a saturation phenomenon occurred in our system. But if it did occur at pressures less than approximately 0.1 torr, the values we used for very low CO_2 pressures are probably too high. We compared the integrated absorptance of a few samples of $\text{CO}_2 + \text{N}_2$ in which the CO_2 pressure was determined by expansion to some previous results¹ for ² samples with shorter paths and higher CO_2 pressures which could be measured accurately. The integrated absorptance of the earlier samples was usually slightly greater than that of present samples having the same absorber thickness and equivalent pressure. Therefore, it seems likely that there were small systematic errors, possibly due to adsorption, in the pressures we determined by the expansion method.

In view of the above discussion, the quoted values of CO_2 pressures below 0.1 torr are probably less than 8 percent too high or less than 2 percent too low.

Mixtures of $\text{CO}_2 + \text{N}_2$ or $\text{CO}_2 + \text{A}$ were formed by adding the N_2 or A to the cell after the CO_2 was introduced. Fans installed in the cell were used

to mix the gases. Several different samples, each at a different total pressure, were formed from the same CO_2 . The same mixture was also frequently investigated at four different path lengths: 121, 237, 469, and 933 meters.

The absorber thickness u was calculated by the use of the following equation.

$$u(\text{atm cm})_{\text{STP}} = (1 + 0.005p) p L 273/296, \quad (2-1)$$

where L is the geometrical path length in cm and p is the partial pressure of CO_2 in atm. The term $(273/296)$ accounts for the difference in density between standard temperature (273°K) and room temperature (296°K) at which the measurements were made. The quantity $(1 + 0.005p)$, which accounts for the non-linearity in the relation between the density of CO_2 and its pressure, is negligible except for pressures greater than approximately 1 atm. It could be neglected for samples included in the present study, but it has been included in a computer program used to calculate sample parameters for pressures as high as 15 atm.

When working with mixtures of $\text{CO}_2 + \text{N}_2$, it is convenient to use an equivalent pressure P_e which is proportional to the half-width of the absorption lines, regardless of the composition of the mixture. We have found that such an equivalent pressure is given by

$$P_e = 1.3 p + (P - p), \quad (2-2)$$

where P is the total pressure, and p is the partial pressure of CO_2 . It is noted that P_e approaches P for a very dilute mixture of CO_2 in N_2 ($p \ll P$).

Table 2-1 includes the parameters for 116 samples of CO_2 and $\text{CO}_2 + \text{N}_2$. The CO_2 partial pressure p , the total pressure P , and the equivalent pressure P_e are given in torr and in atm. Also included are references to the transmittance curves and the integrated absorptance tables. Samples of $\text{CO}_2 + \text{A}$ which are discussed in Section 3.3 were scanned only over the region above 2400 cm^{-1} and are not included in Table 2-1.

2.3 RECORDING AND REDUCTION OF DATA

A spectrum of each sample was scanned over a sufficiently wide region that there was essentially no absorption at the starting and end points. Spectral curves called background curves were scanned over the same spectral regions with the cell evacuated. The shapes of the background curves varied with the number of passes of the cell because of the variation in reflectivity with wavenumber. Therefore, it was necessary to scan background curves at the same paths as those used for the samples.

TABLE 2-1
SAMPLE PARAMETERS

Sam. No.	p	P	P _e	p	P	P _e
	torr	torr	torr	atm	atm	atm
1	742	742	969	0.976	0.976	0.275
2	742	742	969	0.976	0.976	0.275
3	208	208	271	0.274	0.274	0.356
4	742	742	969	0.976	0.976	1.28
5	101	101	131	0.133	0.133	0.173
6	208	208	271	0.274	0.274	0.356
7	208	740	803	0.274	0.974	0.0563
8	51.5	51.5	67.0	0.0678	0.0678	0.0881
9	101	101	131	0.133	0.133	0.173
10	208	208	271	0.274	0.274	0.356
11	208	740	803	0.274	0.974	1.06
12	51.5	51.5	67.0	0.0678	0.0678	0.0881
13	208	208	271	0.274	0.274	0.356
14	208	740	803	0.274	0.974	1.06
15	26.8	26.8	34.8	0.0353	0.0353	0.0459
16	26.8	229	237	0.0353	0.301	0.312
17	26.7	26.7	34.7	0.0351	0.0351	0.0457
18	2.7	229	237	0.0351	0.301	0.312
19	3.20	3.20	4.16	0.00421	0.00421	0.00547
20	26.7	26.7	34.7	0.0351	0.0351	0.0457
21	26.7	229	237	0.0351	0.301	0.312
22	3.20	3.20	4.16	0.00421	0.00421	0.00547
23	3.20	10.9	11.9	0.00421	0.0143	0.0156
24	3.20	32.9	33.9	0.00421	0.0433	0.0446
25	3.20	103	104	0.00421	0.136	0.137
26	0.80	0.80	1.04	0.00105	0.00105	0.00137
27	3.20	3.20	4.16	0.00421	0.00421	0.00547
28	3.20	10.9	11.9	0.00421	0.0143	0.0156
29	3.20	32.5	33.5	0.00421	0.0428	0.0440
30	3.20	103	104	0.00421	0.136	0.137
31	0.80	0.80	1.04	0.00105	0.00105	0.00137
32	3.20	3.20	4.16	0.00421	0.00421	0.00547
33	3.20	10.9	11.9	0.00421	0.0143	0.0156
34	3.20	32.5	33.5	0.00421	0.0428	0.0440
35	3.20	103	104	0.00421	0.136	0.137
36	0.400	0.400	0.520	0.000526	0.000526	0.000684
37	0.400	1.00	1.12	0.000526	0.00132	0.00147
38	0.400	3.20	3.32	0.000526	0.00421	0.00437
39	0.400	15.0	15.1	0.000526	0.0197	0.0199
40	0.400	100	100.1	0.000526	0.132	0.132

TABLE 2-1 (cont.)

Sam. No.	L Path m	u atm cm STP	Fig. in which spectral curve appears	Tables of integrated absorptance
1	933	84,400	3-1	4-1
2	469	42,400	3-1	4-1
3	933	23,600	3-1	4-1
4	237	21,400	3-1	4-1
5	933	11,400	3-1	4-1
6	469	11,900	3-1	4-1
7	469	11,900	3-1	4-1
8	933	5,830	3-1	4-1
9	469	5,750	3-1	4-1
10	237	5,990	3-1	4-1
11	237	5,990	3-2	4-1
12	469	2,930	3-2	4-1
13	121	3,060	3-2	4-1
14	121	3,060	3-2	4-1
15	469	1,530	3-2	4-1
16	469	1,530	3-2	4-1
17	237	768	3-2	4-2
18	237	768	3-2	4-2
19	933	362	3-2	4-2
20	121	392	3-2	4-2
21	121	392	3-3	4-2
22	469	182	3-3	4-2
23	469	182	3-3	4-2
24	469	182	3-3	4-2
25	469	182	3-3	4-2
26	933	90.6	3-3	4-2
27	237	92.0	3-3	4-2
28	237	92.0	3-3	4-2
29	237	92.0	3-3	4-2
30	237	92.0	3-3	4-2
31	469	45.5	3-3	4-2
32	121	47.0	3-3	4-2
33	121	47.0	3-3	4-2
34	121	47.0	3-3	4-2
35	121	47.0	3-3	4-2
36	469	22.8	3-4	4-3
37	469	22.8	3-4	4-3
38	469	22.8	3-4	4-3
39	469	22.8	3-4	4-3
40	469	22.8	3-4	4-3

TABLE 2-1
SAMPLE PARAMETERS

Sam. No.	p	P	P _e	p	P	P _c
	torr	torr	torr	atm	atm	atm
41	0.100	0.100	0.130	0.000132	0.000132	0.000171
42	0.200	0.200	0.260	0.000263	0.000263	0.000342
43	0.400	0.400	0.520	0.000526	0.000526	0.000684
44	0.400	1.00	1.12	0.000526	0.00132	0.00147
45	0.400	3.20	3.32	0.000526	0.00421	0.00437
46	0.400	15.0	15.1	0.000526	0.0197	0.0199
47	0.400	100.0	100.1	0.000526	0.132	0.132
48	0.051	0.051	0.066	0.000067	0.000067	0.000087
49	0.100	0.100	0.130	0.000132	0.000132	0.000171
50	0.200	0.200	0.260	0.000263	0.000263	0.000342
51	0.400	0.400	0.520	0.000526	0.000526	0.000684
52	0.400	1.00	1.12	0.000526	0.00132	0.00147
53	0.400	3.20	3.32	0.000526	0.00421	0.00437
54	0.400	15.0	15.1	0.000526	0.0197	0.0199
55	0.400	100.0	100.1	0.000526	0.132	0.132
56	0.025	0.025	0.033	0.000033	0.000033	0.000043
57	0.025	0.054	0.062	0.000033	0.000071	0.000081
58	0.025	0.114	0.122	0.000033	0.000150	0.000160
59	0.025	0.294	0.302	0.000033	0.000387	0.000397
60	0.025	0.723	0.731	0.000033	0.000951	0.000961
61	0.025	1.88	1.89	0.000033	0.00247	0.00248
62	0.025	5.25	5.26	0.000033	0.00691	0.00692
63	0.025	14.5	14.5	0.000033	0.0191	0.0191
64	0.025	39.0	39.0	0.000033	0.0513	0.0513
65	0.025	100.0	100.0	0.000033	0.132	0.132
66	0.012	0.012	0.016	0.000016	0.000016	0.000021
67	0.025	0.025	0.033	0.000033	0.000033	0.000043
68	0.025	0.054	0.062	0.000033	0.000071	0.000081
69	0.025	0.114	0.122	0.000033	0.000150	0.000160
70	0.025	0.294	0.302	0.000033	0.000387	0.000397
71	0.025	0.723	0.731	0.000033	0.000951	0.000961
72	0.025	1.88	1.89	0.000033	0.00247	0.00248
73	0.025	5.25	5.26	0.000033	0.00691	0.00692
74	0.025	14.5	14.5	0.000033	0.0191	0.0191
75	0.025	39.0	39.0	0.000033	0.0513	0.0513
76	0.025	100.0	100.0	0.000033	0.132	0.132
77	0.0055	0.0055	0.0072	0.000033	0.000033	0.0000094
78	0.012	0.012	0.016	0.000016	0.000016	0.000021
79	0.025	0.025	0.033	0.000033	0.000033	0.000043
80	0.025	0.054	0.062	0.000033	0.000071	0.000081

TABLE 2-1 (cont.)

Sam. No.	L Path m	u atm cm STP	Fig. in which spectral curve appears	Tables of integrated absorbance
41	933	11.3	3-4	4-3
42	469	11.4	3-4	4-3
43	237	11.5	3-4	4-3
44	237	11.5	3-4	4-3
45	237	11.5	3-4	4-3
46	237	11.5	3-4	4-3
47	237	11.5	3-4	4-3
48	933	5.8	3-4	4-3
49	469	5.69	3-4	4-3
50	237	5.75	3-4	4-3
51	121	5.87	3-4	4-3
52	121	5.87	3-4	4-3
53	121	5.87	3-4	4-3
54	121	5.87	3-4	4-3
55	121	5.87	3-4	4-3
56	933	2.8	3-4	4-4
57	933	2.8	3-4	4-4
58	933	2.8	3-4	4-4
59	933	2.8	3-4	4-4
60	933	2.8	3-4	4-4
61	933	2.8	3-4	4-4
62	933	2.8	3-4	4-4
63	933	2.8	3-4	4-4
64	933	2.8	3-4	4-4
65	933	2.8	3-4	4-4
66	933	1.4	3-5	4-4
67	469	1.4	3-5	4-4
68	469	1.4	3-5	4-4
69	469	1.4	3-5	4-4
70	469	1.4	3-5	4-4
71	469	1.4	3-5	4-4
72	469	1.4	3-5	4-4
73	469	1.4	3-5	4-4
74	469	1.4	3-5	4-4
75	469	1.4	3-5	4-4
76	469	1.4	3-5	4-4
77	933	0.62	3-5	4-5
78	469	0.68	3-5	4-5
79	237	0.72	3-5	4-5
80	237	0.72	3-5	4-5

TABLE 2-1
SAMPLE PARAMETERS

Sam. No.	p	P	P _e	p	P	P _e
	torr	torr	torr	atm	atm	atm
81	0.025	0.114	0.122	0.000033	0.000150	0.000160
82	0.025	0.294	0.302	0.000033	0.000387	0.000397
83	0.025	0.723	0.731	0.000033	0.000951	0.000961
84	0.025	1.88	1.89	0.000033	0.00247	0.00248
85	0.025	5.25	5.26	0.000033	0.00691	0.00692
86	0.025	14.5	14.5	0.000033	0.0191	0.0191
87	0.025	39.0	39.0	0.000033	0.0513	0.0513
88	0.025	100.0	100.0	0.000033	0.132	0.132
89	0.0055	0.0055	0.0072	0.0000072	0.0000072	0.0000094
90	0.012	0.012	0.016	0.000016	0.000016	0.000021
91	0.025	0.025	0.033	0.000033	0.000033	0.000043
92	0.025	0.054	0.062	0.000033	0.000071	0.000081
93	0.025	0.114	0.122	0.000033	0.000150	0.000160
94	0.025	0.294	0.302	0.000033	0.000387	0.000397
95	0.025	0.723	0.731	0.000033	0.000951	0.000961
96	0.025	1.88	1.89	0.000033	0.00247	0.00248
97	0.025	5.25	5.26	0.000033	0.00691	0.00692
98	0.025	14.5	14.5	0.000033	0.0191	0.0191
99	0.025	39.0	39.0	0.000033	0.0513	0.0513
100	0.025	100.0	100.0	0.000033	0.132	0.132
101	0.0055	0.0055	0.0072	0.0000072	0.0000072	0.0000094
102	0.012	0.012	0.016	0.000016	0.000016	0.000021
103	0.012	0.126	0.130	0.000016	0.000166	0.000171
104	0.012	0.384	0.388	0.000016	0.000505	0.000510
105	0.012	1.20	1.20	0.000016	0.00158	0.00158
106	0.012	3.45	3.45	0.000016	0.00454	0.00454
107	0.012	10.2	10.2	0.000016	0.0134	0.0134
108	0.012	32.5	32.5	0.000016	0.0428	0.0428
109	0.012	100.4	100.4	0.000016	0.132	0.132
110	0.0055	0.0055	0.0072	0.0000072	0.0000072	0.0000094
111	0.0055	0.197	0.199	0.0000072	0.000259	0.000261
112	0.0055	0.600	0.602	0.0000072	0.000789	0.000792
113	0.0055	1.89	1.89	0.0000072	0.00249	0.00249
114	0.0055	8.51	8.51	0.0000072	0.0112	0.0112
115	0.0055	29.5	29.5	0.0000072	0.0388	0.0388
1.6	0.0055	102	102	0.0000072	0.134	0.134

TABLE 2-1 (cont.)

Sam. No.	L Path m	u atm cm STP	Fig. in which spectral curve appears	Tables of integrated absorptance
81	237	0.72	3-5	4-5
82	237	0.72	3-5	4-5
83	237	0.72	3-5	4-5
84	237	0.72	3-5	4-5
85	237	0.72	3-5	4-5
86	237	0.72	3-5	4-5
87	237	0.72	3-5	4-5
88	237	0.72	3-5	4-5
89	469	0.31	3-5	4-5
90	237	0.35	3-5	4-5
91	121	0.37	3-5	4-5
92	121	0.37	3-5	4-5
93	121	0.37	3-5	4-5
94	121	0.37	3-5	4-5
95	121	0.37	3-5	4-5
96	121	0.37	3-6	4-5
97	121	0.37	3-6	4-5
98	121	0.37	3-6	4-5
99	121	0.37	3-6	4-5
100	121	0.37	3-6	4-5
101	237	0.16	3-6	4-6
102	121	0.18	3-6	4-6
103	121	0.18	3-6	4-6
104	121	0.18	3-6	4-6
105	121	0.18	3-6	4-6
106	121	0.18	3-6	4-6
107	121	0.18	3-6	4-6
108	121	0.18	3-6	4-6
109	121	0.18	3-6	4-6
110	121	0.081	3-6	4-6
111	121	0.081	3-6	4-6
112	121	0.081	3-6	4-6
113	121	0.081	3-6	4-6
114	121	0.081	3-6	4-6
115	121	0.081	3-6	4-6
116	121	0.081	3-6	4-6

Each spectrum was examined and compared with others as a check for consistency. Small corrections were made to account for spurious deflections and for absorption by H_2O and CO impurities in the sample. The transmittance was determined from the ratio of the deflection on the sample curve to the deflection on the background curve at the same wavenumber. Each spectral curve then was replotted and digitized by the method described previously.³ Pairs of values related to transmittance and wavenumber were punched on IBM cards which served as input for a computer program used to calculate transmittance and integrated absorbance as a function of wavenumber. The replotted spectra are shown in Section 3 and tables of integrated absorbance appear in Section 4.

SECTION 3

RESULTS AND DISCUSSION

3.1 TRANSMISSION SPECTRA

Curves of transmittance versus wavenumber are shown in Figs. 3-1 through 3-6 for the 116 samples of CO_2 and $\text{CO}_2 + \text{N}_2$ listed in Table 2-1. The curves were replotted from the original curves obtained with a spectral resolution of approximately 2.5 cm^{-1} . Small corrections were made to account for absorption by CO near 2140 cm^{-1} and by H_2O from 2800 to 2870 cm^{-1} and from 1815 to 1870 cm^{-1} .

Table 3-1 includes a list of absorption bands expected in this region. Evidence of many of them can be seen in the transmission spectra, although most of the absorption is due to the very strong 00^0_1 band and two medium strength bands, 11^1_0 and 03^1_0 . Features of several of the bands listed in Table 3-1, as well as others not listed, can probably be identified in spectra with higher resolution which we plan to obtain.

TABLE 3-1

CO₂ ABSORPTION BANDS BETWEEN 1800 AND 2800 cm⁻¹

Band Center cm ⁻¹		Upper Level	Lower Level*	Molecular Species ⁺
1846.29		05 ¹ 0	02 ² 0	
1886.	H	04 ⁰ 0	01 ¹ 0	
1896.00		05 ¹ 0	02 ⁰ 0	
1917.67		04 ² 0	01 ¹ 0	
1932.5	H	03 ¹ 0		
2003.5		12 ⁰ 0	01 ¹ 0	
2004.01		13 ¹ 0	02 ² 0	
2053.72		13 ¹ 0	02 ⁰ 0	
2076.5	H	11 ¹ 0		
2094.		12 ² 0	01 ¹ 0	
2137.	H	20 ⁰ 0	01 ¹ 0	
2165.30		21 ¹ 0	02 ² 0	
2215.01		21 ¹ 0	02 ² 0	
2327.48		02 ⁰ 1	02 ⁰ 0	
2336.66		01 ¹ 1	01 ¹ 0	
2349.3	H	00 ⁰ 1		
2429.41		10 ⁰ 1		
2500.42		04 ⁰ 0		C ¹² O ¹⁶ O ¹⁸
2548.33		04 ⁰ 0 PI		
2614.24		12 ⁰ 0		C ¹² O ¹⁶ O ¹⁸
2670.90		12 ⁰ 0 PI		
2757.04		20 ⁰ 0		C ¹² O ¹⁶ O ¹⁸
2797.02		20 ⁰ 0 PI		

H denotes that the position of the band center is from Herzberg⁵; all others were calculated from energy levels given by Stull, Wyatt and Plass⁶.

* Lower level is 00⁰0 unless indicated otherwise.

+ All species are the C¹²O¹⁶O¹⁶ molecule except as noted.

PI denotes pressure-induced bands.

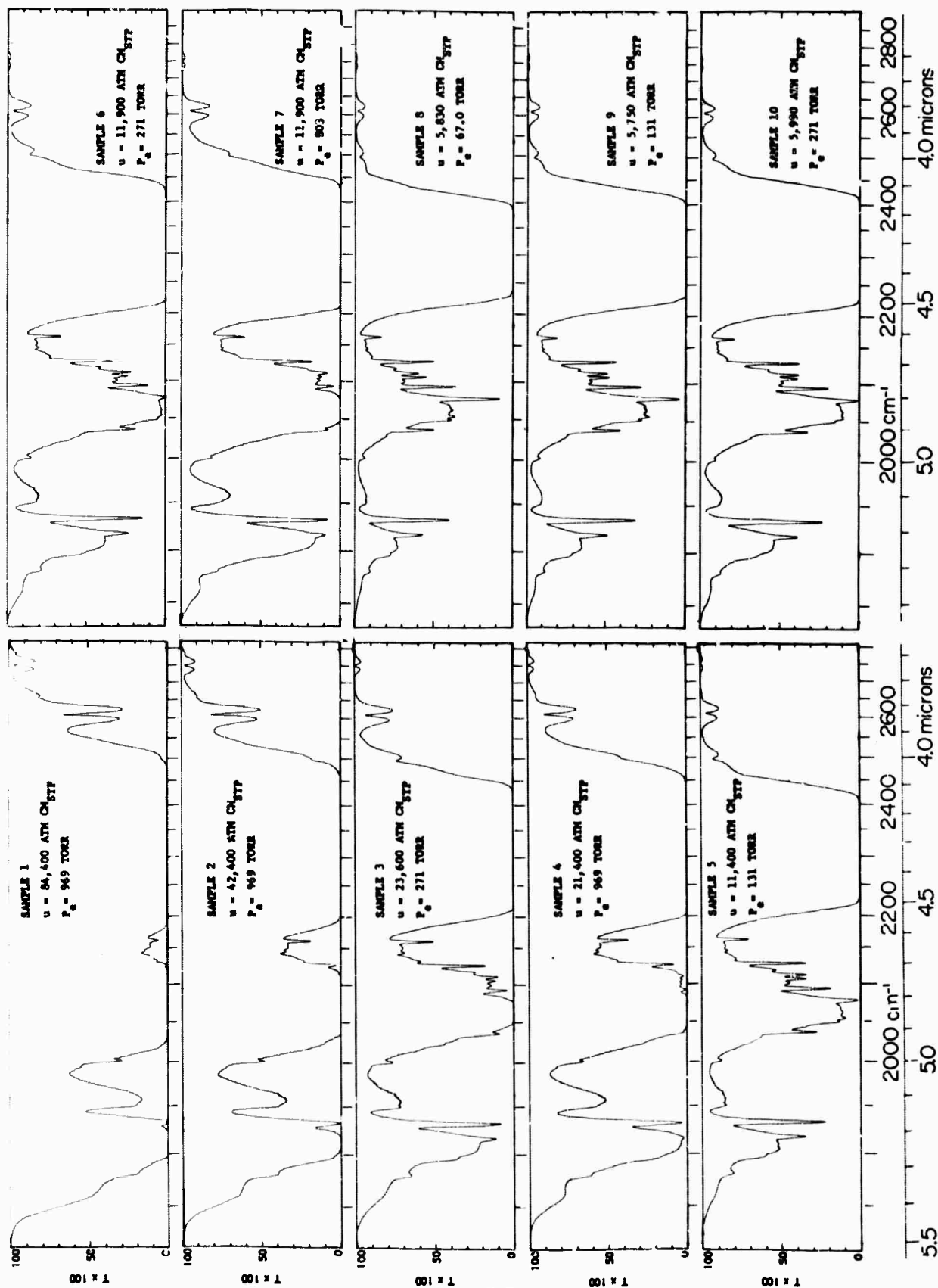


Fig. 3-1

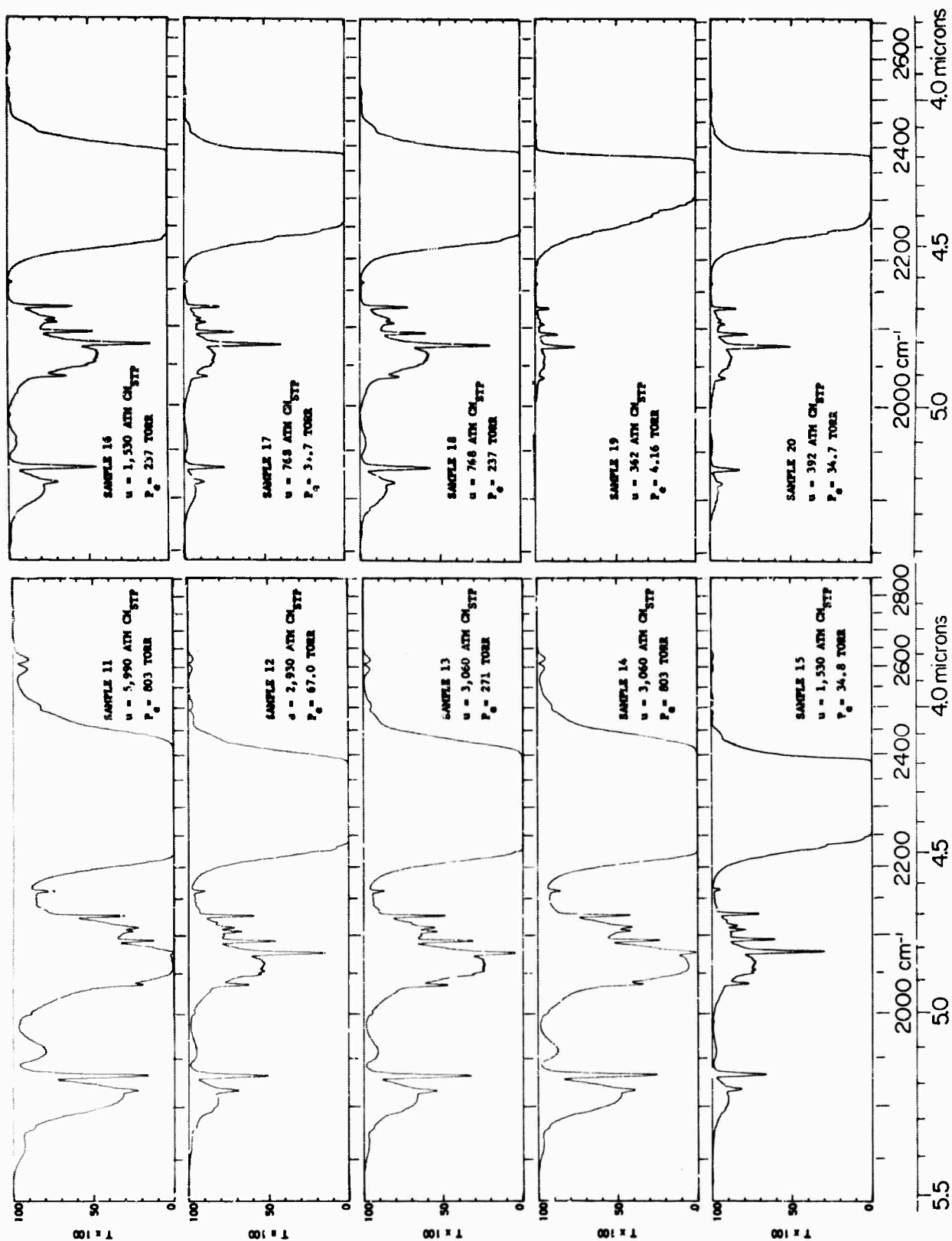


Fig. 3-2

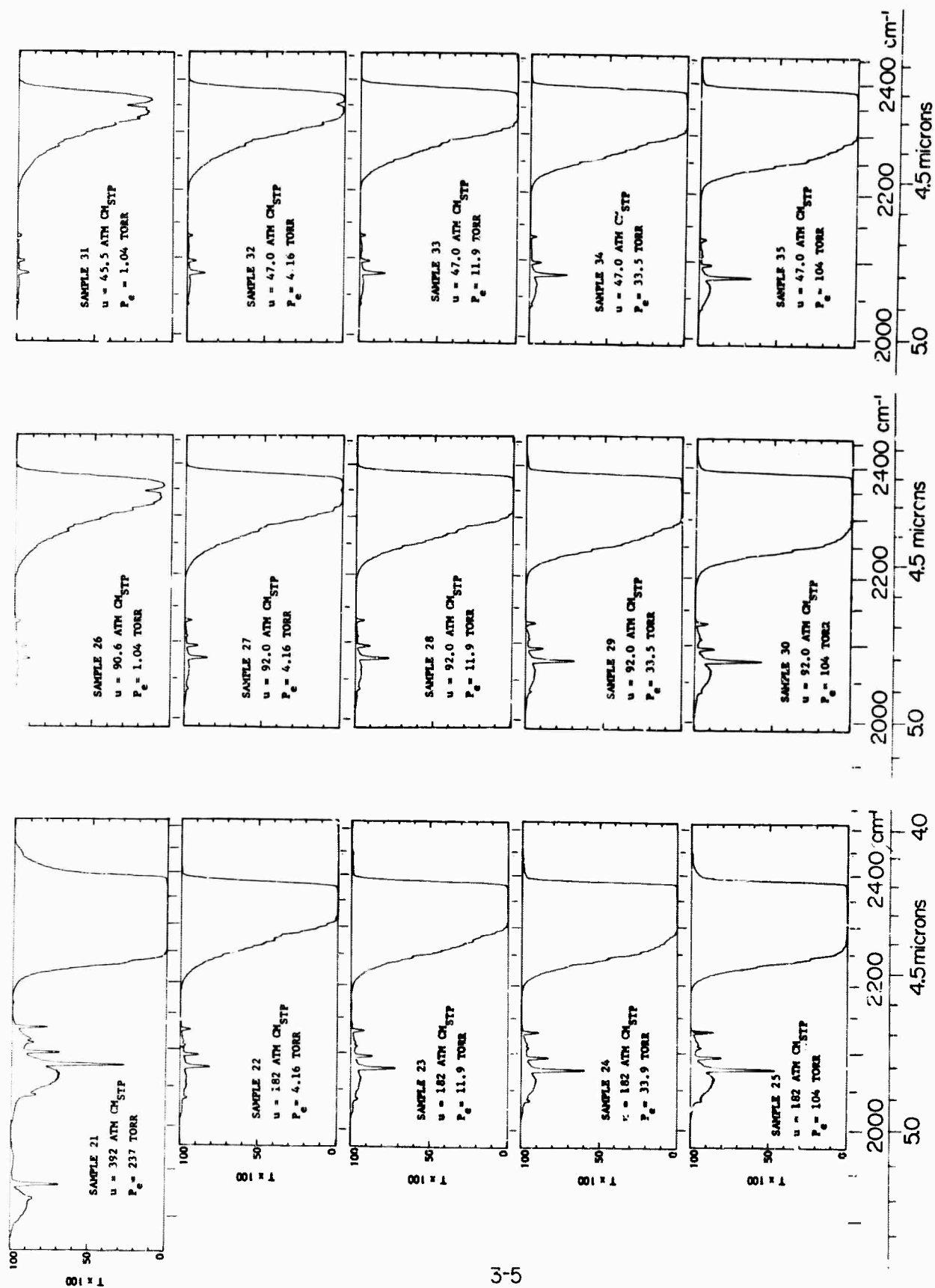


Fig. 3-3

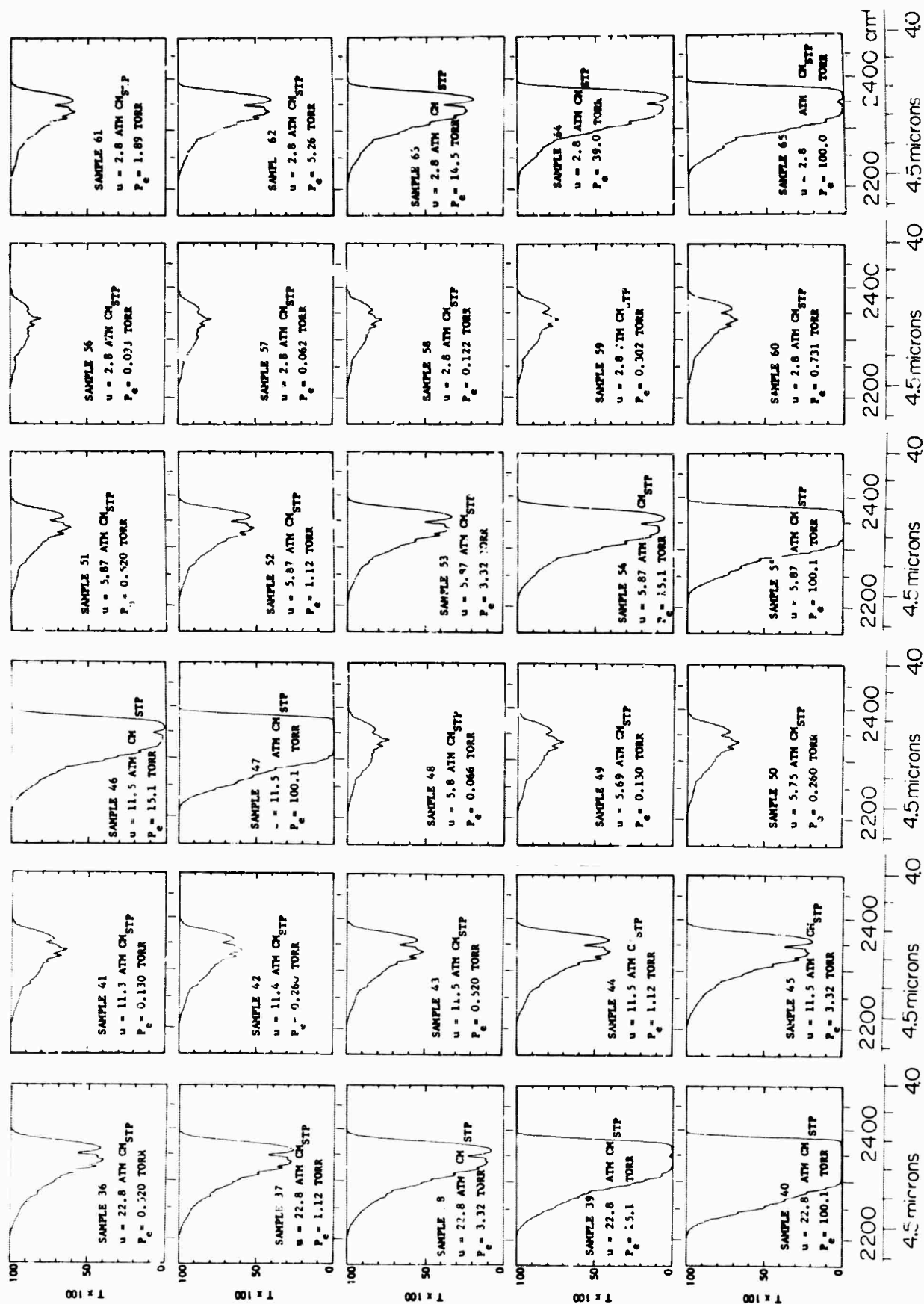


Fig. 3-4

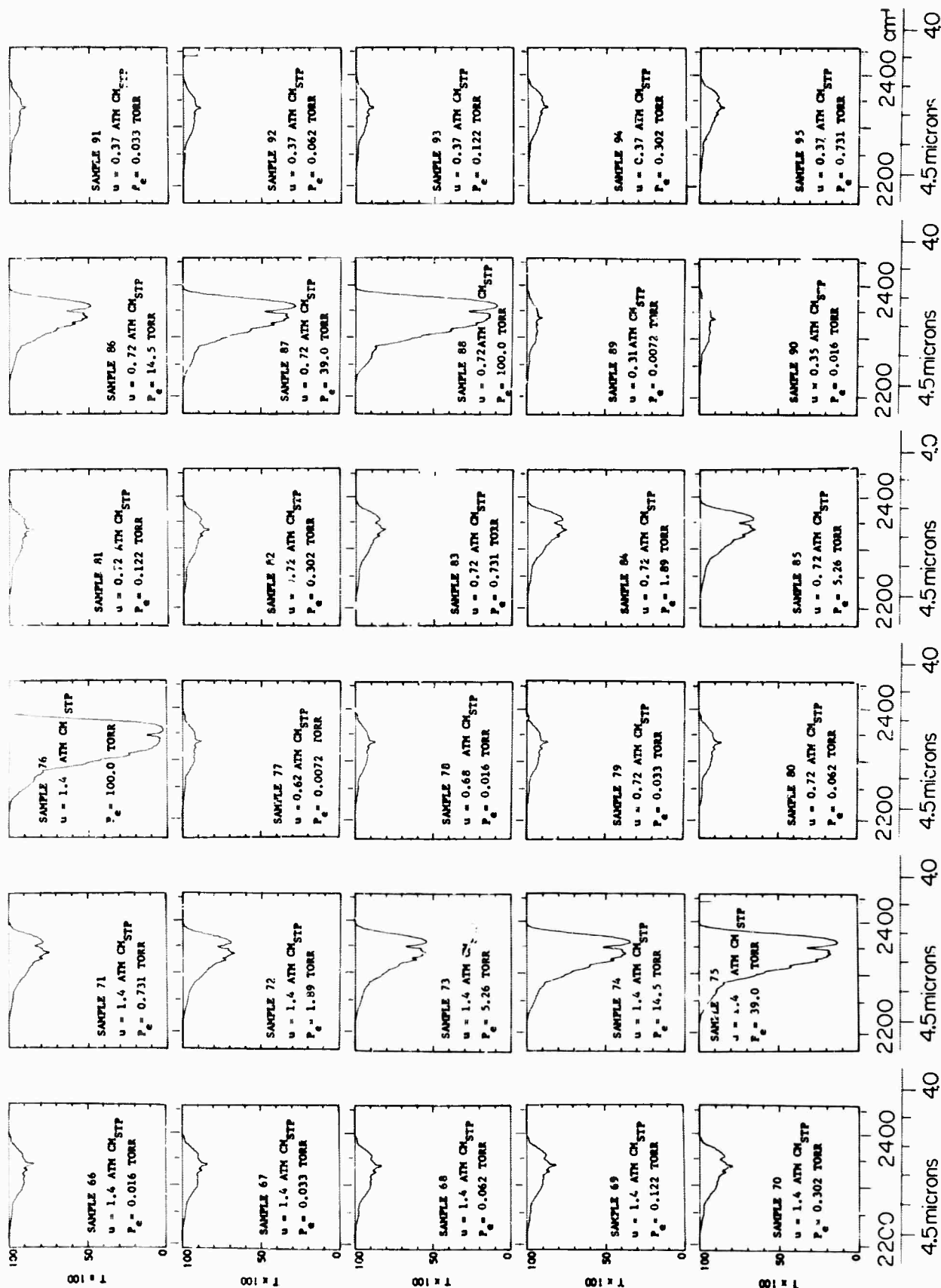


Fig. 3-5

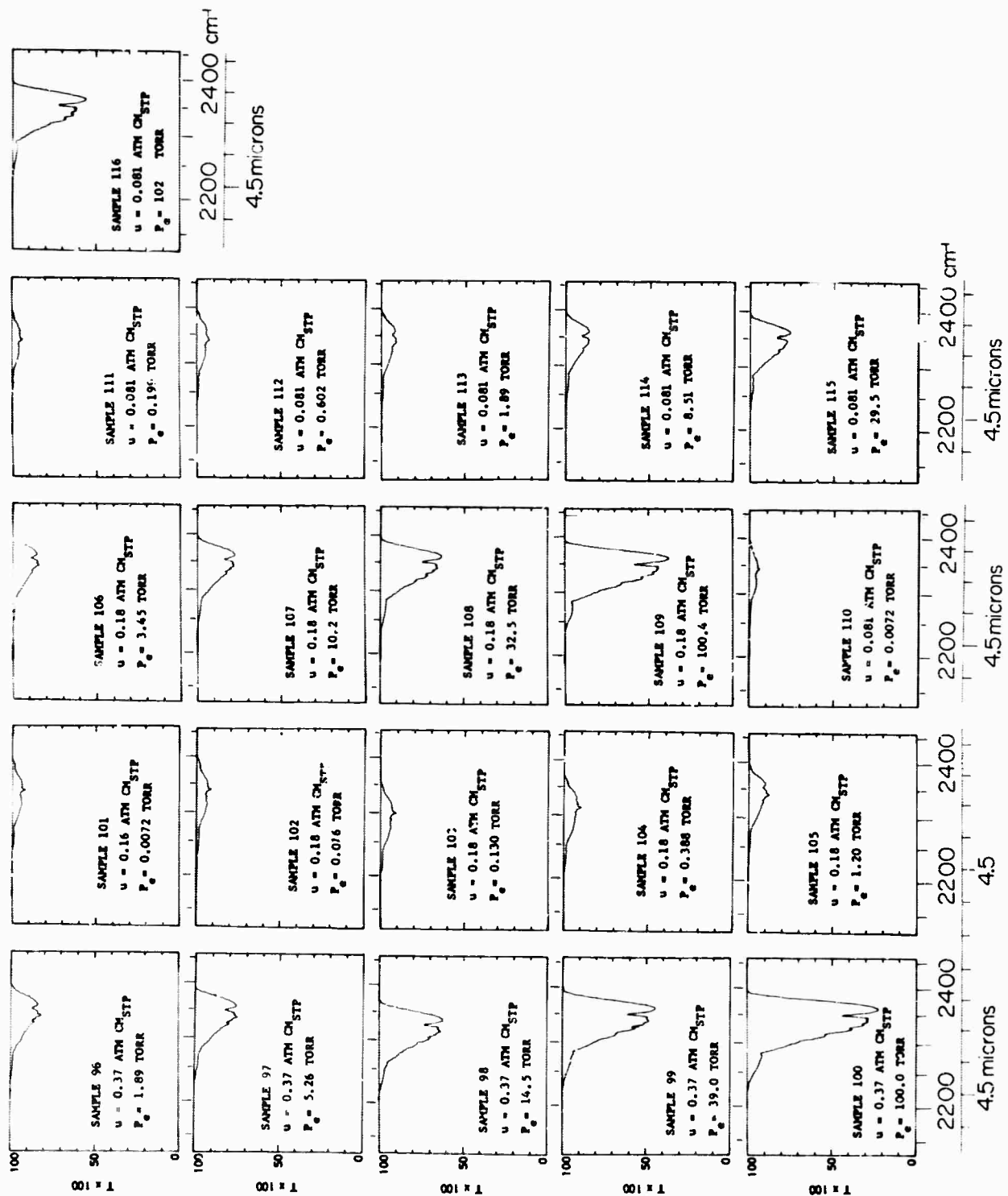


Fig. 3-6

3.2 INTEGRATED ABSORPTANCE

The integrated absorptance over the region from 2190 to 2425 cm^{-1} is plotted versus P_e on log-log scales in Fig. 3-7 for Samples 36 through 116. Each solid curve corresponds to the value of absorber thickness indicated. The broken curve with slope of 0.5 has been included for comparison with the other curves. The integrated absorptance of a band composed of non-overlapping strong lines having the Lorentz line shape is proportional to $(uP_e)^{0.5}$. (A strong line is essentially opaque over a region a few times as wide as the width of the line.) The $(uP_e)^{0.5}$ dependence would give rise to a curve of slope 0.5 on the log-log plot in Fig. 3-7. We see that the slopes of several of the curves are slightly less than 0.5 for pressures between 10 and 100 torr. The deviation from the $(uP_e)^{0.5}$ relationship for pressures greater than 10 torr is due to overlapping of the lines and the presence of weak lines. The effect of overlapping is particularly important for the larger values of u .

The slopes of the curves representing the smaller values of absorber thickness are seen to decrease with decreasing pressure. The increased absorptance at low pressure is due to the Doppler broadening of the absorption lines. The Lorentz line shape, which is a good approximation to collision-broadened lines, is quite different from the pressure independent Doppler line shape. The absorption coefficient in the wings of a Doppler shaped line decreases much more rapidly with the distance from the center than does a Lorentz line. Therefore, under certain conditions, the absorption in the wings of a line is due to collision broadening, while Doppler broadening dominates near the line center. Essentially all the absorption by a low pressure sample with very small absorber thickness occurs near the line center; therefore, its integrated absorptance is independent of pressure. However, in the case of a low pressure sample with intermediate absorber thickness, there is appreciable absorption in the wings of the lines where collision broadening is dominant. Therefore, the integrated absorptance is slightly dependent on pressure. The increasing dependence on P_e as u increases can be seen by comparing the slopes of the curves in Fig. 3-7 in the region near $P_e = 0.1$ to r . Plass⁷ has given a theoretical discussion of the absorption by lines in which either Doppler broadening or collision broadening is dominant as well as lines in which both types of broadening make significant contributions.

Figure 3-8 shows the relation between integrated absorptance and absorber thickness for different values of P_e . The curve corresponding to 1000 torr represents data from Burch, Gryvnak, and Williams¹ and is included for comparison. The other curves were cross plotted from the curves in Fig. 3-7. Curves corresponding to absorption by non-overlapping strong lines with the Lorentz shape would be parallel to the comparison line whose slope is 0.5.⁷ Segments of the 10 torr and 100 torr curves are

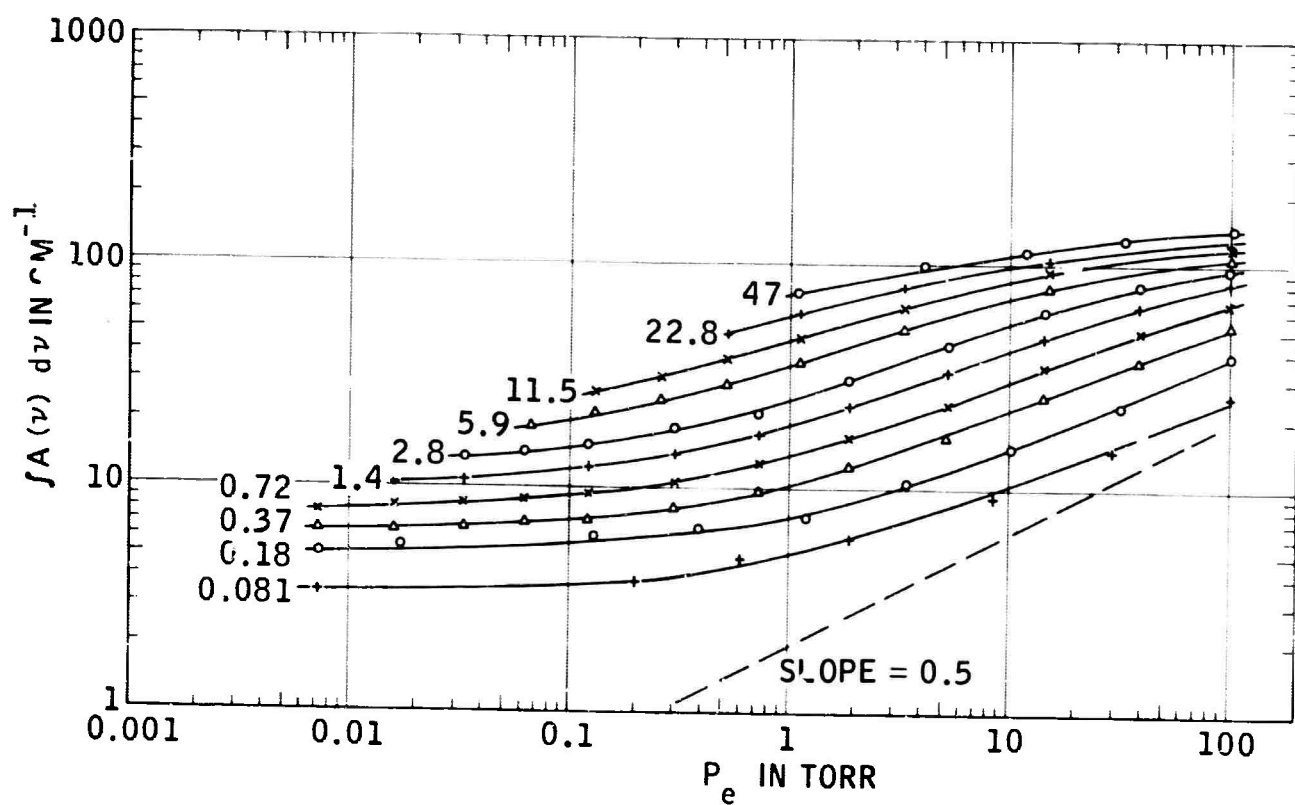


Fig. 3-7 THE INTEGRATED ABSORPTANCE OF THE 2190-2425 cm⁻¹ REGION VERSUS EQUIVALENT PRESSURE.

Each curve corresponds to the indicated value of absorber thickness in atm cm_{STP}. The broken line with slope = 0.5 is shown for comparison.

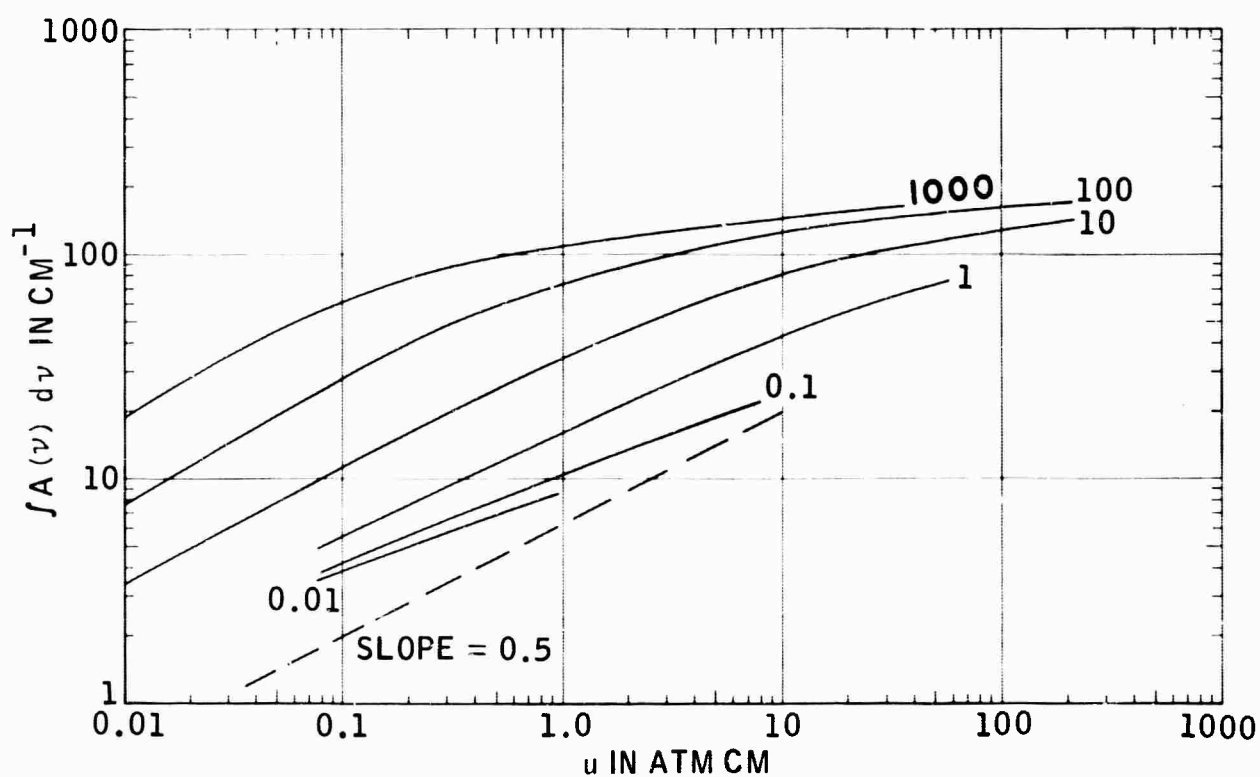


Fig. 3-8 THE INTEGRATED ABSORPTANCE OF THE $2190\text{-}2425\text{ cm}^{-1}$ REGION VERSUS ABSORBER THICKNESS.

Each curve corresponds to the indicated value of equivalent pressure in torr. The broken line with slope = 0.5 is shown for comparison.

seen to be nearly parallel to the comparison line, indicating that integrated absorptance is approximately proportional to $u^{0.5}$ for the values of u and P_e represented.

The relation between the integrated absorptance and the parameter uP_e is shown in Fig. 3-9. The integrated absorptance can be expressed as a function of this convenient parameter when the absorption is primarily due to strong lines with the Lorentz shape.⁷ Under this condition, all the curves corresponding to different pressures coincide. Although none of the curves coincide, except when the absorption is nearly complete throughout much of the band, the 1, 10, and 100 torr curves occur near each other for uP_e greater than approximately 10 atm cm_{STP} torr. For smaller values of uP_e at lower pressures, the curves are separated because of Doppler broadening, indicating that the integrated absorptance cannot be related to the single variable uP_e .

3.3 ABSORPTION BETWEEN 2400 AND 2580 cm^{-1}

A few very weak isotopic bands and two pressure-induced bands occur between 2400 and 2580 cm^{-1} , but most of the absorption in this region is due to the extreme wings of the very strong lines of the 00⁰1 band. The centers of all the lines of this band are confined to the region below the band head near 2400 cm^{-1} . We were able to account for the isotopic and pressure-induced bands in the 2400-2580 cm^{-1} region and to determine the amount of absorption by the wings of the strong lines. From the results we were able to derive curves from which the absorptance due to the wings of the strong lines can be determined for samples of CO_2 , $\text{CO}_2 + \text{N}_2$, or $\text{CO}_2 + \text{A}$.

The transmittance $T(\nu)$ at wavenumber ν is related to absorber thickness u and absorption coefficient $K(\nu)$ according to the following equation.

$$T(\nu) = \exp [-K(\nu) u], \quad \text{or} \quad K(\nu) = -\frac{1}{u} \ln T(\nu). \quad (3-1)$$

The total absorption coefficient $K(\nu)$ due to the wings of CO_2 lines broadened by CO_2 and N_2 is given by

$$K(\nu) = \left[p/p^0 \right] K_s^0(\nu) + \left[p_{\text{N}_2}/p^0 \right] K_{\text{N}_2}^0(\nu). \quad (3-2)$$

The quantity $K_s^0(\nu)$ is the self-broadening absorption coefficient which arises from CO_2 - CO_2 collisions when the CO_2 pressure is 1 atm. Similarly, $K_{\text{N}_2}^0(\nu)$ is the N_2 -broadening coefficient due to CO_2 - N_2 collisions when the

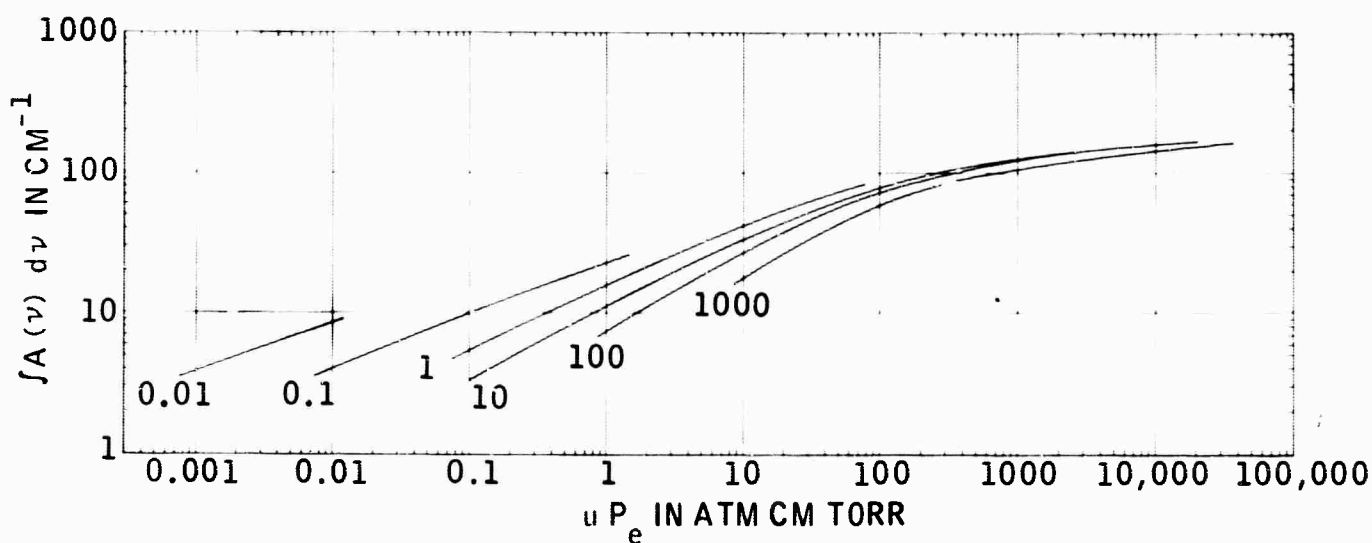


Fig. 3-9 THE INTEGRATED ABSORPTANCE OF THE $2190-2425 \text{ cm}^{-1}$ REGION VERSUS THE PRODUCT OF ABSORBER THICKNESS AND EQUIVALENT PRESSURE.

Each curve corresponds to the indicated value of equivalent pressure.

N_2 partial pressure is 1 atm. The superscripts 0 denote standard pressure, 1 atm. The partial pressures of CO_2 and N_2 in atm are p and p_{N_2} , respectively. Equation (3-2) can be used for mixtures of CO_2 plus N_2 any non-absorbing broadening gas, such as A, by substituting the appropriate broadening coefficient and partial pressure.

Since no line centers occur in this region, except for those in the very weak bands whose absorption was accounted for, there is no unresolved structure within the 2.5 cm^{-1} spectral slitwidth. Therefore, the observed transmittance is a very good approximation to the true transmittance. The absorption coefficient determined from the observed transmittance by the use of Eq. (3-1) also approximates the true coefficient that would be observed with infinite resolution.

Values of the normalized self-broadening coefficient $K_S^0(\nu)$ were determined from several of the larger samples of pure CO_2 by the use of Eqs. (3-1) and (3-2). These values were then substituted in Eq. (3-2) in order to find values of $K_{N_2}^0(\nu)$ and $K_A^0(\nu)$ from samples containing these broadening gases. The results are shown in Fig. 3-10, where each of the normalized absorption coefficients is plotted against wavenumber. Points have not been included in the curves at wavenumbers where there is appreciable absorption by the isotopic and pressure-induced bands. Therefore, these curves represent only the contribution of the wings of strong lines whose centers occur below 2400 cm^{-1} . Winters, Silverman, and Benedict⁸ have made similar measurements in this region. Their work does not extend to wavenumbers as high as ours, but the two sets of results are in good agreement over the region covered by both.

Since the positions, strengths, and widths of the lines are known, it is apparent that considerable information about the shapes of the extreme wings of the lines can be obtained. A report⁹ dealing with the shapes of the lines in this region, as well as in the $1.4\text{ }\mu$ and $2.7\text{ }\mu$ regions is being prepared.

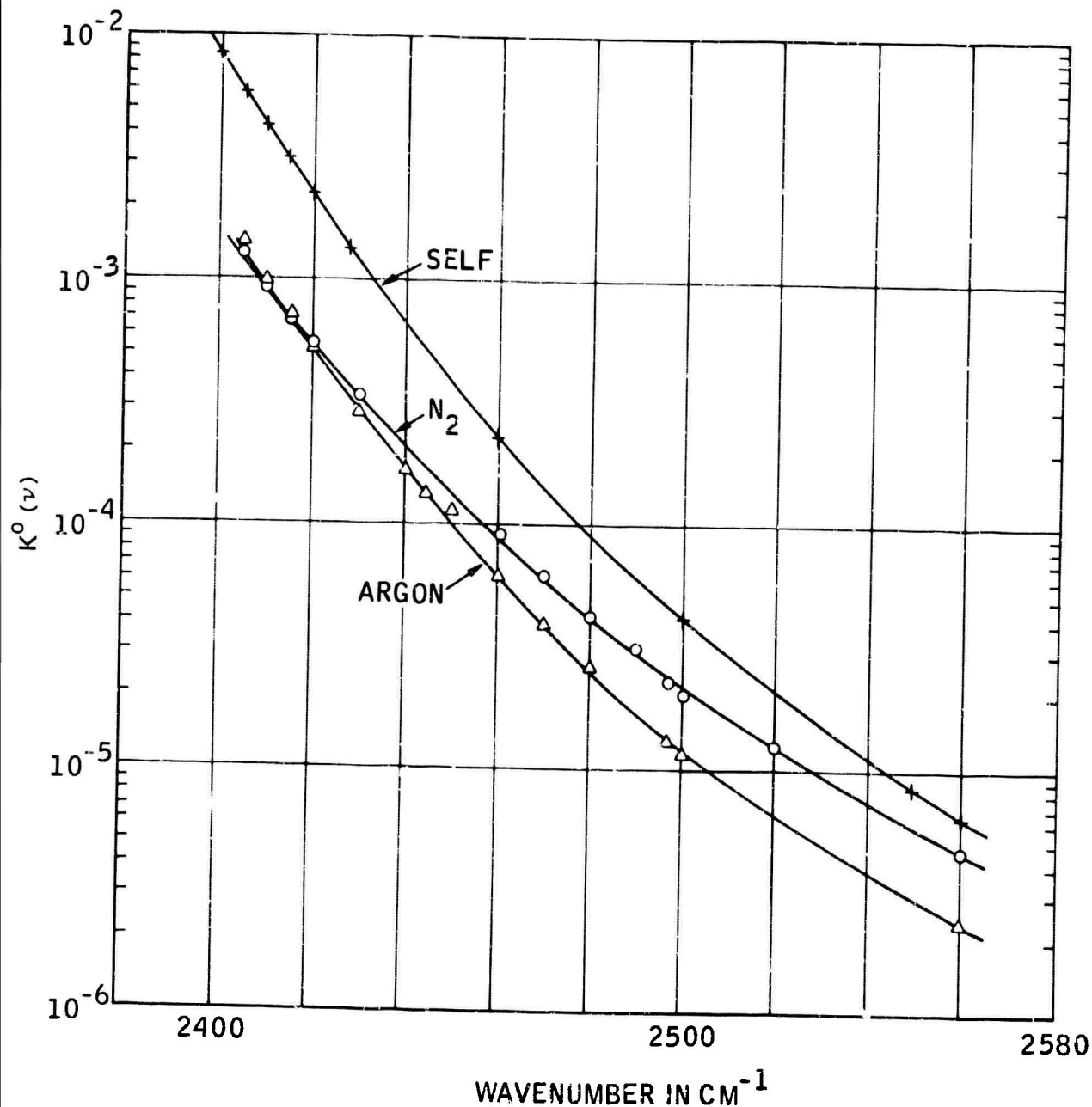


Fig. 3-10 THE NORMALIZED ABSORPTION COEFFICIENT VERSUS WAVENUMBER FOR CO_2 BETWEEN 2400 AND 2580 cm^{-1} .

The upper curve corresponds to self-broadened CO_2 , i.e., pure CO_2 , at 1 atm pressure. The lower two curves correspond to samples of CO_2 diluted in the gases indicated at 1 atm. The curves represent only the contribution of the lines whose centers occur below 2400 cm^{-1} .

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SECTION 4

TABLES OF INTEGRATED ABSORPTANCE

Values of the integrated absorptance $\int_{\nu}^{\nu'} A(\nu) d\nu$ for Samples 1 to 116 are shown in Tables 4-1 to 4-6. The sample number and the parameters are listed at the top of each column along with ν' , the upper limit of integration. The integrated absorptance between any two wavenumbers tabulated is equal to the difference between the values given at those two points.

The integrated absorptance was calculated from values of transmittance which were determined from the spectra at points 1 cm^{-1} apart. This interval is sufficiently small that the original spectra can be reconstructed with little loss of structure by plotting the transmittance values and joining the points with straight lines.

The samples included in the various tables are as follows:

<u>Sample No.</u>	<u>Table</u>
1 to 16	4-1
17 to 35	4-2
36 to 55	4-3
56 to 76	4-4
77 to 100	4-5
101 to 116	4-6

Table 4-1 $\int A(\nu) d\nu$ [illegible]

$$\int_{\gamma} A(z) dz$$
[illegible]

Table 4-2 $\int A(\nu) d\nu$

Table with 26 columns and 100 rows of numerical data. The first column contains labels (e.g., 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260). The subsequent columns contain numerical values, some of which are in scientific notation (e.g., 1.0E-01, 1.0E-02, 1.0E-03, 1.0E-04, 1.0E-05, 1.0E-06, 1.0E-07, 1.0E-08, 1.0E-09, 1.0E-10, 1.0E-11, 1.0E-12, 1.0E-13, 1.0E-14, 1.0E-15, 1.0E-16, 1.0E-17, 1.0E-18, 1.0E-19, 1.0E-20, 1.0E-21, 1.0E-22, 1.0E-23, 1.0E-24, 1.0E-25, 1.0E-26, 1.0E-27, 1.0E-28, 1.0E-29, 1.0E-30, 1.0E-31, 1.0E-32, 1.0E-33, 1.0E-34, 1.0E-35, 1.0E-36, 1.0E-37, 1.0E-38, 1.0E-39, 1.0E-40, 1.0E-41, 1.0E-42, 1.0E-43, 1.0E-44, 1.0E-45, 1.0E-46, 1.0E-47, 1.0E-48, 1.0E-49, 1.0E-50, 1.0E-51, 1.0E-52, 1.0E-53, 1.0E-54, 1.0E-55, 1.0E-56, 1.0E-57, 1.0E-58, 1.0E-59, 1.0E-60, 1.0E-61, 1.0E-62, 1.0E-63, 1.0E-64, 1.0E-65, 1.0E-66, 1.0E-67, 1.0E-68, 1.0E-69, 1.0E-70, 1.0E-71, 1.0E-72, 1.0E-73, 1.0E-74, 1.0E-75, 1.0E-76, 1.0E-77, 1.0E-78, 1.0E-79, 1.0E-80, 1.0E-81, 1.0E-82, 1.0E-83, 1.0E-84, 1.0E-85, 1.0E-86, 1.0E-87, 1.0E-88, 1.0E-89, 1.0E-90, 1.0E-91, 1.0E-92, 1.0E-93, 1.0E-94, 1.0E-95, 1.0E-96, 1.0E-97, 1.0E-98, 1.0E-99, 1.0E-100, 1.0E-101, 1.0E-102, 1.0E-103, 1.0E-104, 1.0E-105, 1.0E-106, 1.0E-107, 1.0E-108, 1.0E-109, 1.0E-110, 1.0E-111, 1.0E-112, 1.0E-113, 1.0E-114, 1.0E-115, 1.0E-116, 1.0E-117, 1.0E-118, 1.0E-119, 1.0E-120, 1.0E-121, 1.0E-122, 1.0E-123, 1.0E-124, 1.0E-125, 1.0E-126, 1.0E-127, 1.0E-128, 1.0E-129, 1.0E-130, 1.0E-131, 1.0E-132, 1.0E-133, 1.0E-134, 1.0E-135, 1.0E-136, 1.0E-137, 1.0E-138, 1.0E-139, 1.0E-140, 1.0E-141, 1.0E-142, 1.0E-143, 1.0E-144, 1.0E-145, 1.0E-146, 1.0E-147, 1.0E-148, 1.0E-149, 1.0E-150, 1.0E-151, 1.0E-152, 1.0E-153, 1.0E-154, 1.0E-155, 1.0E-156, 1.0E-157, 1.0E-158, 1.0E-159, 1.0E-160, 1.0E-161, 1.0E-162, 1.0E-163, 1.0E-164, 1.0E-165, 1.0E-166, 1.0E-167, 1.0E-168, 1.0E-169, 1.0E-170, 1.0E-171, 1.0E-172, 1.0E-173, 1.0E-174, 1.0E-175, 1.0E-176, 1.0E-177, 1.0E-178, 1.0E-179, 1.0E-180, 1.0E-181, 1.0E-182, 1.0E-183, 1.0E-184, 1.0E-185, 1.0E-186, 1.0E-187, 1.0E-188, 1.0E-189, 1.0E-190, 1.0E-191, 1.0E-192, 1.0E-193, 1.0E-194, 1.0E-195, 1.0E-196, 1.0E-197, 1.0E-198, 1.0E-199, 1.0E-200, 1.0E-201, 1.0E-202, 1.0E-203, 1.0E-204, 1.0E-205, 1.0E-206, 1.0E-207, 1.0E-208, 1.0E-209, 1.0E-210, 1.0E-211, 1.0E-212, 1.0E-213, 1.0E-214, 1.0E-215, 1.0E-216, 1.0E-217, 1.0E-218, 1.0E-219, 1.0E-220, 1.0E-221, 1.0E-222, 1.0E-223, 1.0E-224, 1.0E-225, 1.0E-226, 1.0E-227, 1.0E-228, 1.0E-229, 1.0E-230, 1.0E-231, 1.0E-232, 1.0E-233, 1.0E-234, 1.0E-235, 1.0E-236, 1.0E-237, 1.0E-238, 1.0E-239, 1.0E-240, 1.0E-241, 1.0E-242, 1.0E-243, 1.0E-244, 1.0E-245, 1.0E-246, 1.0E-247, 1.0E-248, 1.0E-249, 1.0E-250, 1.0E-251, 1.0E-252, 1.0E-253, 1.0E-254, 1.0E-255, 1.0E-256, 1.0E-257, 1.0E-258, 1.0E-259, 1.0E-260, 1.0E-261, 1.0E-262, 1.0E-263, 1.0E-264, 1.0E-265, 1.0E-266, 1.0E-267, 1.0E-268, 1.0E-269, 1.0E-270, 1.0E-271, 1.0E-272, 1.0E-273, 1.0E-274, 1.0E-275, 1.0E-276, 1.0E-277, 1.0E-278, 1.0E-279, 1.0E-280, 1.0E-281, 1.0E-282, 1.0E-283, 1.0E-284, 1.0E-285, 1.0E-286, 1.0E-287, 1.0E-288, 1.0E-289, 1.0E-290, 1.0E-291, 1.0E-292, 1.0E-293, 1.0E-294, 1.0E-295, 1.0E-296, 1.0E-297, 1.0E-298, 1.0E-299, 1.0E-300, 1.0E-301, 1.0E-302, 1.0E-303, 1.0E-304, 1.0E-305, 1.0E-306, 1.0E-307, 1.0E-308, 1.0E-309, 1.0E-310, 1.0E-311, 1.0E-312, 1.0E-313, 1.0E-314, 1.0E-315, 1.0E-316, 1.0E-317, 1.0E-318, 1.0E-319, 1.0E-320, 1.0E-321, 1.0E-322, 1.0E-323, 1.0E-324, 1.0E-325, 1.0E-326, 1.0E-327, 1.0E-328, 1.0E-329, 1.0E-330, 1.0E-331, 1.0E-332, 1.0E-333, 1.0E-334, 1.0E-335, 1.0E-336, 1.0E-337, 1.0E-338, 1.0E-339, 1.0E-340, 1.0E-341, 1.0E-342, 1.0E-343, 1.0E-344, 1.0E-345, 1.0E-346, 1.0E-347, 1.0E-348, 1.0E-349, 1.0E-350, 1.0E-351, 1.0E-352, 1.0E-353, 1.0E-354, 1.0E-355, 1.0E-356, 1.0E-357, 1.0E-358, 1.0E-359, 1.0E-360, 1.0E-361, 1.0E-362, 1.0E-363, 1.0E-364, 1.0E-365, 1.0E-366, 1.0E-367, 1.0E-368, 1.0E-369, 1.0E-370, 1.0E-371, 1.0E-372, 1.0E-373, 1.0E-374, 1.0E-375, 1.0E-376, 1.0E-377, 1.0E-378, 1.0E-379, 1.0E-380, 1.0E-381, 1.0E-382, 1.0E-383, 1.0E-384, 1.0E-385, 1.0E-386, 1.0E-387, 1.0E-388, 1.0E-389, 1.0E-390, 1.0E-391, 1.0E-392, 1.0E-393, 1.0E-394, 1.0E-395, 1.0E-396, 1.0E-397, 1.0E-398, 1.0E-399, 1.0E-400, 1.0E-401, 1.0E-402, 1.0E-403

Table 4-3 $\int A(v) dv$ [illegible]

Table 4-4 $\int A(\nu) d\nu$ [illegible]

Table 4-5 $\int A(\nu) d\nu$

Lat. (°N)	Long. (°E)	Alt. (m)	Temp. (°C)	Sal. (psu)	Density (kg/m³)	Speed (m/s)	Direction (°)	Wave Hs (m)	Wave T (s)	Wave Dir (°)	Wind S (m/s)	Wind Dir (°)	Pressure (hPa)	Humidity (%)	Clouds (%)	Visibility (km)	Sea State
76	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
77	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
78	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
79	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
80	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
81	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
82	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
83	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
84	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
85	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
86	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
87	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
88	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
89	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
90	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
91	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
92	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
93	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
94	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
95	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
96	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
97	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
98	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
99	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
100	120.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Table 4-6 $\int_v^v \dot{A}(v) dv$ [illegible]

SECTION 5

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(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Applied Research Laboratories Aeronutronic Division Philco-Ford Corporation		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE Absorption by CO ₂ Between 1800 and 2850 cm ⁻¹ (3.5-5.6 Microns)			
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5. AUTHOR(S) (Last name, first name, initial) Gryvnak, David A. Burch, Darrell E. Patty, Richard R. Miller, Earl E.			
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13. ABSTRACT Transmission spectra in the 1800-2850 cm ⁻¹ region have been obtained for more than 100 samples of CO ₂ and CO ₂ mixed with N ₂ and A. The spectral resolution was 2.5 cm ⁻¹ . Sample pressures varied from 0.0055 to 742 torr with absorber thicknesses covering the range from 0.081 to 84,400 atm cm. Spectra of several samples at the lower pressures show the effect of Doppler broadening. Measurements in the 2400-2560 cm ⁻¹ region provide information about the absorption by the extreme wings of collision-broadened lines. Replotted transmission spectra and extensive tables of integrated absorptance for 116 samples are included.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
CO ₂						
Infrared						
Absorption						
Doppler Broadening						
Collision Broadening						

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